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Metal oxide-based chemo-resistive nanostructured gas sensors for environment and human safety: a review

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Abstract

Industrialization and its progress are very important for the economy and to move towards prosperity, stimulating innovation and creating jobs. Nonetheless, industrialization has negative impacts, if not done judiciously, such as pollution, increased greenhouse gas emissions and global warming. Therefore, amenity-with-security is of fundamental significance in a new and dynamic lifestyle. A gas sensor is one of the crucial devices for monitoring and subsequently preserving the clean atmosphere among a number of other safety technologies. In-depth assessments of gas sensors and their necessity in the environment (air) pollution are provided in the current review. With a special emphasis on metal oxide semiconductor (MOS)-based gas sensors, the study of gas sensors and the factors relating to sensing mechanisms. It not only describes the basic concepts and brief history of gas sensors,

Keywords: nanomaterial, sensitivity, gas sensor, Metal Oxide Semiconductor (MOS) etc

Introduction

Nanotechnology is defined as any technology on a nanoscale (less than 100 nm) that has applications in recent and modern advances. In general, nanotechnology is concerned with the development of materials, electronics, or other structures having at least one dimension ranging from 01 - 100 nanometer. In other words, it is the shaping and reshaping of structures, devices, and systems at the Nano scale for design, characterization, production, and application.

In the second half of the twenty-first century, nanotechnology has emerged as a significant field alongside Information technology, cellular and molecular biology, and semiconductor technology. The study of nanotechnology within the realm of science and technology has brought forth innovative ideas and advancements in various areas, including materials and manufacturing, nanoelectronics, the medical industry etc. Many believe that nanotechnology has the potential to initiate the following industrial revolution. Nanometer-scale characteristics are mostly composed of its elemental elements.

Nanomaterials

Nanomaterials are exceedingly tiny, with a minimum of one dimension of 100 nanometer or less. Such substances are sometimes nanoscale in one dimension, two dimensions & three dimensions. Common nanomaterials include fullerenes, nanotubes, dendrimers, and quantum dots.

Nanomaterials are used in nanotechnology and possess unique physical and chemical characteristics from ordinary chemicals (for example, silver Nano, etc).

Zero-dimensional, one-dimensional, two-dimensional & three-dimensional nanostructures are categories for materials with nanostructures.

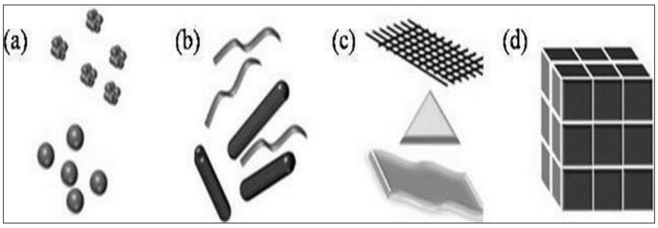

Fig 1: Nanomaterial classification in.(a) 0 D, (b) 1 D, (c) 2 D and (d) 3 D

Properties of nanomaterials

Size, morphology & nanoparticle content can be altered to alter nanomaterials' properties. Grain structure has a considerable influence on the various material qualities such as electrical, mechanical, optical, thermal, catalytic, and so on. When the particle size decreases from bulk to nano, the characteristics alter. Depending on the production method, nanostructured materials can take the shape of thin films, quantum wells, quantum dots, powder, and so on. All nanomaterials are made up of grains, which are invisible to the naked human eye. A nanocrystalline substance has grains with sizes ranging from 1 to 100nm.

Physical properties

The crystal structure of nanoparticles is the same as that of bulk particles, but with differing lattice properties. The melting point of nanoparticles varies with their size. The surface-to-volume ratio phenomena influences nanoparticle reactivity and solubility. They can be employed in technologies such as adhesion, lubrication, and stabilization.

Optical properties

When a substance is on the nanoscale, it has a different wavelength at which light absorption begins than when it is in its bulk form. As a result, the size and type of material have a large impact on light absorption. Because nanoparticles are particles that are smaller than the wavelength of visible light., light scattering over them is anticipated to be minimal.

Electronic properties

Quantum confinement occurs when a particle's size is decreased to a nanoscale level by reducing dimensions on one or more sides. The energy bands are subsequently converted into discrete energy levels, which increases or widens the band gap and so increases band gap energy.

Mechanical properties

Crystalline materials' hardness normally increases when crystal size decreases & hence their mechanical toughness is strong. At nanoscale, ceramic & metallic substances can display this behaviour.

Thermal properties

Because the nanoscale influences the atoms on the surface of the particles, the melting point of the nanoparticles drops when compared to the identical materials on a larger scale. This is because of the fact that atom motion occurs when temperatures are lower in nanoscale.

Chemical properties

When The particle size has been decreased to nanoscale, surface area to volume ratio increases, and so does chemical reactivity. This occurs because the majority of chemical changes occur on the surface. Surfactants may be present in the environment alter the surface and interfacial characteristics.

Need of gas sensors

Detecting hazardous gases in the air is critical for protecting the safety of humans, plants, and animals, as these gases can cause health problems and interfere with industrial or medical procedures. Gas detection equipment, which are generally used for worker safety and plant protection, are critical in detecting dangerous gas concentrations, sounding alarms, and taking countermeasures to avoid hazardous situations. Gas detection systems can be portable or fixed installations, with system dependability and sensor quality being critical considerations in assuring an area's safety. Fixed placed sensors must tolerate severe temperatures, humidity, outside elements, electromagnetic disturbances, and vibrations while retaining accurate measurements in a variety of environmental situations. There is a clear overlap between gas detection technology and process instrumentation.

Gas sensors

A gas sensor is a device that detects the presence of gas monitors gas concentration with which It makes contact with. The breakdown voltage of gas i.e. defected by gas sensors are distinctive for a given gas; thus, the breakdown voltage of the gas is measured by the gas sensor to identify it. Gas concentration is determined by the device's current discharge. These are transducers that Gas molecules are detected & an electrical signal proportional to their concentration is generated.

Industrious revolution contributed significantly to raising the living standards of the next generation. For the welfare of society, industrialization necessitates specific gas detection and monitoring. Emissions of these polluting gases into the environment endanger community health. Result i.e. In order to take the appropriate actions to manage the pollution, it is necessary to evaluate the level of pollution in the atmosphere. Monitoring of both useful and flammable/hazardous gases is in high demand. Various gas sensors have been created to monitor various gases & Many of them are available commercially. gas detectors are extremely valuable within a variety of disciplines, including business, medicine, science, and the environment, where gas can be both hazardous and beneficial. A sensor is built around a sensitive substance. The sensitive material in traditional Taguchi sensors is porous sintered ceramic body.

Materials for sensing

The semiconductor metal oxides, including both n-Type and p-Type oxides, utilised as sensing components for gas sensors. Metal oxides are among the most prevalent, inclusive, and most certainly largest classes of materials due to their extensive structural, physical & chemical properties and functions. Metal Oxides [MO] such as SnO_2, TiO_2 & Others are frequently employed in electronics as sensing layers; however, In real-world gas sensors, ternary and more complicated oxides are also utilized.

Metal oxide semiconductor (MOS) gas sensors are commonly used to identify a variety of hazardous gases, including Ammonia, Nitrogen Dioxide, Hydrogen, Carbon monoxide & volatile organic compounds, to protect the environment as well as human health. Oxides of metals Gas sensors are classified into the two types listed below:

- Transition metal oxides (Fe_2O_3, NiO, Cr_2O_3, and so on).
- Non-transition metal oxides, namely, Pre-transition metal oxides (Al_2O_3, for example) and post-transition metal oxides (ZnO, SnO_2, In_2O_3, e.g.).

Because of their ability to react with various gas molecules, metal oxides are particularly appealing materials for chemical processing. Many gases can be detected by MOS gas sensors. Metal oxide sensors' key advantage is their lengthy service life. There are three primary parts to metal oxide sensors.: measuring devices, electrodes and heating elements.

In this context, the preparation of nanoscale oxide materials seems to be more effective in improving their performance and opening new hopes for their applications in chemical products. By reducing the size of the data to the nanoscale, the ability to recognize data can be greatly improved. In recent years, ZnO nanomaterials have been investigated for the discovery of ZnO due to their electrical strength and thermal stability. However, achieving the high performance and selectivity of ZnO is still a challenge.

Ammonia detection in the environment is a critical issue with ramifications for the environment, clinical practice, the automobile and chemical field. Ammonia sensors have been reviewed, although they no longer employ nanostructures. Thus, ammonia sensitivities in thin films of Zinc Oxide and Zinc Oxide doped with special metals were found to range from 4 to 95 for 1 to 30ppm of NH_3 at temperatures ranging from 30-300^{0}C. Zinc oxide is a key functional material with near-ultraviolet emission, semi conductivity, magnetic characteristics, and piezoelectricity. As a result, Zinc oxide is one of the wide band-gap MO of tremendous interest for a variety of purposes. When at room temperature, zinc oxide exhibits a large band gap of 3.37 eV and a considerable stimulated binding energy of 60 meV.

Analysis of medium gas composition encounters difficulties when using common electrochemical sensors that are entirely reliant on liquid electrolytes, resulting in unexpected failures, for example, as a result of electrolyte drying or when ammonia concentration is high. In such instances, gas sensors based entirely on metallic oxides should be used, notwithstanding their low selectivity and high strength intake. To enhance the efficiency of sensors using metallic-oxide, the heating strategy gas-sensing layer by rapid temperature modulation is presented.

Gas sensor mechanism

These sensors' gas-detecting process involves assimilation of ambient Oxygen on the oxide surface pulls electrons away from the semiconducting material, changing the carrier density and conductivity in the process. Figure depicts a schematic of band bending, demonstrating how, upon contact with oxidizing or reducing gases, the amount of adsorbed oxygen & hence varying conductivity. Calculating the concentration of a gas uses the change in conductivity.

Gas sensors are being employed more frequently in daily life and industrial operations. Because of their exceptional physical & chemical characteristics, minimum cost & straightforward manufacturing processes, metal oxide semiconductor gas sensing materials are preferred. Researchers, however, have not taken into account the gas sensing mechanisms of metal oxide semiconductors, which has led to omissions and mistakes in the interpretation of gas sensing mechanisms in many studies. This review groups, describes, and divides into two categories a number of popular metal oxide semiconductor gas sensing techniques. These mechanisms' range and connection are made clear. Additionally, to emphasize the significance of the gas sensing properties of MOS, this paper chooses four techniques for improving them. It also assesses the gas sensing processes.

Gas sensor characteristics and sensor development

Sensitivity

Sensitivity is a feature of a sensor that shows a change in the gas-detecting material's chemical or physical characteristics when exposed to gas. Resistance variation or any other metric that changes in response to a slight concentration change are used to measure it. The sensitivity of film is largely dependent on its thickness, operating temperature, pressure, presence of another gas, and so on.

$$\text{Sensitivity} = \frac{\text{Resistance to Change}}{\text{change in concentration}}$$

The level of sensitivity should be as high as feasible.

Selectivity

A gas sensor's capacity to distinguish a specific gas from a mixture of gases referred to as selectivity. It is essential in the identification of gases. Its primary application is in industry.

Stability

Stability is a measure of repeatability over time under the same circumstances, this implies that the sensor need to deliver the same outcome for a specific stimulation after a lengthy period of time.

Response time

This is the device's operating speed. It is the period of time that passes before the characteristic parameter reaches a specific percentage of its maximum value for a particular gas concentration. A sensor with a short response time is preferable.

Recovery time

The amount of time until the sensor resistance reaches 70% of its saturated value after the sensor has been exposed to gas. A good sensor should recover quickly so that it can be put to use again.

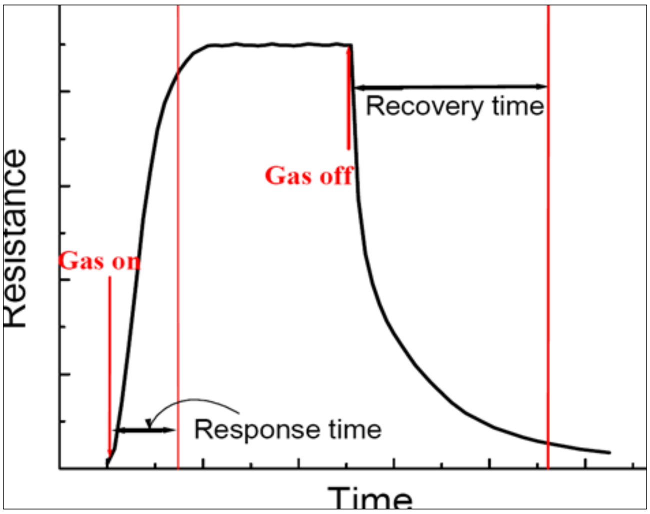

Fig 1: Resistance vs. time response and recovery analysis

The presence of various gases for e.g. toxic, flammable and combustible gases could be identified using sensor devices. These devices were consumed by abundant industries such as power stations, transportation, chemicals, food and beverage and metals. Sensors are based on tested technology, new procedures of production are empowering lesser, lower power, and more choosy sensors. In addition to actual size and length scales, the surface and bulk properties and differences between those properties play a noteworthy role in gas sensing applications shown in table-1.

Table 1: Discussion of different types of sensor parameters with different materials

	Sensor							
	Class 1		Class 2		Class 3		Class 4	
Parameters	**CNT**	**MOS**	**Polymer Chemiresistor**	**Chem FET**	**Piezo electric (SAW)**	**SPR**	**Chromatography**	**Emission Spectroscopy**
Selectivity	+	+	+	+	-	- -	++	++
Sensitivity	+	+	+	+	+	+	+	+
Power saving	+	-	-	+	+	++	+	+
Low cost	+	+	+	+	+	- -	- -	- -
Noise efficiency	+	-	- -	+	+	+	+	+
Size miniaturization	+++	++	++	+	+	+	-	-
High response time	++	+	+	+	+	+	- -	+

CNT- Carbon Nano tube, MOS-Metal Oxide Semiconductor, Chem FET- Field Effect Transistor with a solid electrolyte as the gate material, SAW-Surface Acoustic Wave, SPR-Surface Plasma Resonance

Note: The negative (-) sign indicates a disadvantage and the positive (+) one indicates an advantage for the sensor at the corresponding parameter.

Research plans & methodology

Metal oxide nanomaterials with a large surface area have great interest of scientists due to their uses in electronics i.e. nanoelectronics. The nanomaterial has antibacterial, antifungal, antioxidant, and cancer-fighting properties. These materials can be made using a variety of processes, including chemical vapour condensation, arc discharge, hydrogen plasma-metal interaction, and laser pyrolysis in the vapour phase. There are also other methods employed, including solid-state ball milling, liquid-state microbiological processes, micro-emulsions, and sol- gel synthesis.

The synthesis process has a notable effect on the attributes and possible applications of nanoparticles. MO nanoparticles have numerous characteristics, and their potential applications appear to be numerous and diverse.

Conclusions and future perspectives

We summarize the research progress of gas sensors metal oxides, and their composites as sensitive materials. The gas sensing mechanism, main factors affecting sensing performance, and the Applications of various gas sensors are presented and discussed in detail. It can be concluded that the metal oxide-based nanostructure gas sensor can efficiently identify and detect toxic and harmful gases. Compared with pure metal oxide semiconductors, composite materials have higher carrier rates, larger high mechanical strength, and large specific surface area, and the synergistic effect of the two components can further enhance the gas sensing performance. Composite metal oxide materials during the composite process of the material, but also give more active sites for the gas sensing process, thereby further improving the gas sensing performance. In addition, the composite materials can effectively reduce the working temperature.

Nanomaterial-based gas sensors have made great progress in the past few decades, the operating temperature of metal oxides is too high, and the selectivity of 2D materials is still unsatisfactory. In the future, effective strategies such as building composite structures are highly needed to improve the selectivity, reduce the operating temperature, and improve the sensitivity and other properties. In addition, the research on the combination of metal oxides with 2D materials is still at an early stage, and its sensing mechanisms of the composite-based gas sensors should be further studied. Only when the mechanism and process are clear, the preparation and assembly of nanomaterial-based gas sensors can be achieved purposefully. In addition, researchers must develop new design strategies to further optimize metal oxide nanomaterials with 2D nanomaterials to make them more suitable for gas sensing. Finally, it is expected that facile assembly and fabrication processes will be developed to enable batch fabrication of gas sensors with high stability, selectivity, sensitivity, reproducibility, and quick response in the future.

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